

STAT

The Action, of Ultrasonics, On Agar Agar Solutions

(Part 4 of 'The Influence of Ultrasonic Waves on
High-Molecular Compounds'))

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"The Action, of Ultrasonics, On Agar Agar Solutions (Representing Part 4 of 'The Influence of Ultrasonic Waves On High-Molecular Compounds')"

by SOBUE Hiroshi and ISHIKAWA Kinzō (Source: Nihon Kagaku Zasshi, '0, 11-12 pp 456-8 (Dec '49).

Although Szalay (1), Thieme (2), Sata (3), and Ono (4) have studied the effects of supersonic waves on hydrophilic colloids, as yet insufficient studies of such effects on agar solutions have been conducted. The authors, in order to fill this gap, have conducted experiments on the action of supersonic waves on agar solutions with particular attention to their action on viscosity change, the reduction ^{group} ~~radical~~ of the internal structure of agar, and the sulfate ester ^{group} ~~sulfate radical~~. [Note: 'supersonics' is used in the meaning of 'ultrasonics'.]

PROCEDURE

An agar base culture manufactured by Takeda was boiled for 30 minutes at 95 degrees Centigrade and the residual portion removed with a glass filter.

The supersonic wave generator built in our laboratory utilized the piezo crystal effect. The crystal was 50 millimeters in diameter and 5 millimeters thick with a Kawanishi C-204 oscillator tube. The frequency was approximately 560 kilocycles. 100 cubic centimeters of the agar culture was placed in a test tube 40 millimeters in diameter and a crystalline plate was placed 40 millimeters above the agar. The tube was submerged in an insulating oil so that practically all of the agar was immersed. To determine the absolute magnitude of the supersonic wave amplitude, the anode current was maintained constant at 140 milliamperes so as to give an oil spout of constant height during the reaction. Viscosity measurements were made with the Ostwald viscometer at a temperature of 20 degrees Centigrade plus or minus 0.05 degrees Centigrade. The quinhydrone electrode apparatus was used to determine pH.

Agar solution samples of 0.046, 0.07, 0.092, and 0.14 percent concentrations were prepared and their viscosities determined. However, the concentrations of these samples differ from those of gelatine samples because the concentrations of the agar samples were determined by correlating the jellying action at low concentration, which was considerably greater than that of gelatine, and agar particles combine more firmly with a greater amount of water. Reaction was carried out at five-minute intervals in order to protect the agar solution from the heating effects of cavitation and to prevent the fatiguing of the oscillating portions. Throughout the experiment the insulating oil was cooled by circulating water. After five minutes of sustained reaction, the agar temperature was approximately 20 degrees Centigrade (room temperature: 15 degrees Centigrade). As a result the slight rise in the temperature of the agar, in comparison with similar experiments on other polymer compounds, is not significant.

Table I shows the relative viscosities of the agar which in general decreased exponentially.

TABLE I

Concen- tration in %	Reaction time in min. →	0	5	10	20	35	55
0.14		3.43	2.68	2.27	1.85	1.63	1.52
0.09 ₂		2.23	1.78	1.55	1.37	1.27	1.23
0.07		1.82	1.58	1.48	1.34	1.20	1.15
0.04 ₆		1.49	1.32	1.23	1.15	1.11	1.08

TABLE II

Percentage Decrease of Viscosity $(N_0 - N_t)/N_0 \times 100$ N_0 : Initial relative viscosity N_t : Final relative viscosity [Note: 'N' is used here instead of the original Greek letter 'eta', η]

Concentration in % η	Reaction time in min. \rightarrow	5	10	20	35	55
0.14		21.7	33.8	45.7	52.4	55.5
0.09 ₂		20.2	30.2	38.4	43.0	44.3
0.07		13.1	18.6	26.2	34.0	36.6
0.04 ₆		11.0	17.2	22.4	25.2	27.2

According to Tables I and II no marked decrease of the relative viscosities could be recognized such as was observed by Schmid (6) in his work with such colloid polymers as polystyrene. This might be attributed to the difference between his work and the present experiment in the amplitude of the supersonic waves, but in this case, it might have been largely due to the difference in the state of the solute particles.

The marked rate of decrease of relative viscosity is explained by accelerated particle collisions which occur when the distance of the random movements of the particles is influenced by the amplitude of the supersonic wave and the concentration and shape of the solute particles. The concentration, showing the maximum rate of decrease of relative viscosity as was clearly demonstrated by Thieme's experiment on the gelatins, was determined. In our experiment, the greater the concentration the greater the rate of decrease.

In general, however, since the destructive action of the supersonic waves on the jellying action was slight, it is believed that the maximum decrease of viscosity in the agar solution existed just prior to the formation of the gel structure.

TABLE III
pH Values

Concen- tration in % \downarrow	Reaction time in min. \rightarrow	0	5	10	20	35	55
0.14		4.7 ₈	4.5 ₈	4.4 ₂	4.2 ₃	4.0 ₃	3.6 ₄
0.09 ₂		4.9 ₈	4.4 ₃	4.2 ₅	3.7 ₄	3.5 ₁	3.3 ₀
0.07		4.8 ₇	4.5 ₈	4.2 ₄	4.0 ₃	3.6 ₆	3.3 ₄
0.04 ₆		4.9 ₀	4.6 ₃	4.2 ₈	3.9 ₉	3.4 ₅	3.1 ₄
H ₂ O		4.7 ₂	4.3 ₃	3.9 ₇	3.5 ₄	3.4 ₁	3.1 ₃

The pH values resulting from the experiment are shown in Table III. Specimens subjected to 55 minutes of reaction showed considerably small values between 3.5 and 3.2. pH values were again determined 24 hours later but there was no discernible change.

It has been known that the pH values decrease markedly when agar is autoclaved and hydrolysis is carried out, but in this experiment distilled water was acted upon by the supersonic waves and in each case the decrease of pH was greater than that of the agar solution. It became apparent that the decrease of pH was the result of the generation of HNO_3 and HNO_2 by the action of the supersonic waves on the N_2 of the atmosphere and not of the break up of agar.

Some forms, such as spheroids or micelle-shaped hydrophile colloids, largely recovered their original state when they were allowed to settle after being subjected to the effects of supersonic waves. The various agar solution specimens were allowed to settle for 24 hours (at room temperature of approximately 15 degrees Centigrade) and their viscosity again determined. Since the specimens had slightly solidified they were shaken lightly before viscosity measurements were made again.

TABLE IV

Concen- tration in %	Reaction time in min.	0	5	10	20	35	55
0.14		-0.7 ₅	-1.8 ₆	-2.2 ₀	+1.0 ₈	+4.3 ₅	+5.3 ₁
0.09 ₂		-0.5 ₃	-3.2 ₆	-4.1 ₂	-0.9 ₅	+3.2 ₄	+9.3 ₅
0.07		-0.4 ₉	-0.7 ₆	-2.9 ₀	-2.0 ₈	+0.3 ₃	+4.8 ₅
0.04 ₆		-0.9 ₄	-3.0 ₂	-2.1 ₉	-1.3 ₀	-0.5 ₄	+0.02

Table IV shows the rate of change of viscosity after the specimens were allowed to settle for 24 hours. Minus indicates decrease and plus indicates increase.

The agar exhibited completely different properties from that of the gelatins, which showed remarkable recovery phenomenon. Specimens of high concentration, subjected for shorter lengths of time than those of lower concentration, began to show viscosity recovery sooner than specimens of low concentration which showed recovery only after an extended settling time.

Inorganic acids most affected the viscosity of agar solution; the cation neutralized the charge on the agar particles and the anion acted as an anhydride agent. Although the anhydride action of the charged particles is reversible, the anhydrides that have lost their charges are irreversible and agar particles that have lost their charges form insoluble precipitates upon becoming anhydrides.

The HNO_3 , HNO_2 , and H_2O_2 which form gradually under the action of the supersonic waves, the dissolution of particle clusters formed by the mechanical action arising from the formation of HNO_3 , H_2O_2 , and HNO_2 , and the disturbance of the hydration layers all combine to result in a strong anhydride phenomenon when the reaction time is short. As the reaction time is increased, it is believed, the hydration phenomenon gradually becomes more marked. In this case since the supersonic wave time reaction is increased as the concentration of the specimen is increased, the points at which the changes occur appear in a relatively short time.

The measurement of the reducing ^{group}~~radical~~ arising from the destruction of the agar molecule from the action of the supersonic waves was made by the Micro Bertrand method. Although each specimen was measured after 5, 15, 30, and 60 minutes of reaction, results were negative after 5 minutes; extremely minute quantities were observed after 15 and 30 minutes; and only after 60 minutes were minute measureable quantities obtained. Complete measurements could not be made; however, as the reaction time was increased, detectable quantities could be observed sufficiently.

It is thought that the destructive action of the supersonic waves on soluble particles can be attributed to cavitation, friction between solutes and solvents, collisions, various chemical reactions, and heat; however, the generation of soluble particles ceases when the pressure of cavitation increases, and upon decreasing the pressure of cavitation the generation of soluble particles appears along with the spouting phenomenon and decavitation. In order to observe the effects of cavitation, supersonic waves were directed upon material whose pressure was reduced to 30 millimeters.

TABLE VI

Reaction time (Min)	0	5	15	30
Relative viscosity	2.02	1.99	1.99	1.98

The results are shown in Table VI and indicate a further drop in viscosity. This is because the destruction of the agar particle and the conglomerate form is lessened by the friction between the

solute and solvent. The results are identical with those obtained by Freundlich (7). The greater part of the decrease in viscosity of agar solution stems from cavitation, but perhaps a part was played by Storke's friction.

CONCLUSION

1. When agar solution was subjected to supersonic waves and allowed to settle for 24 hours, viscosity change decreased in specimens subjected to short reaction time, and specimens subjected to long reaction time showed recovery phenomenon.
2. The hydrogen ion concentration varies because of the generation of HNO_3 and HNO_2 . The destructive action resulting from supersonic waves on agar particles is caused not by the sulfate radical but by the generation of the reduction radical which is produced in minute amounts, other radicals being produced in large amounts.
3. Although cavitation was guarded against and decreases of viscosity occurred in spite of this, the viscosity decrease can still be attributed mainly to cavitation.

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